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# REFRACTIVE INDEX, ABSORPTION, WAVE-LENGTH, & ROTATORY POWER, IN RELATION TO MOLECULAR STRUCTURE

ADAM HILGER LTD

SECOND EDITION.

# REFRACTIVE INDEX
## ABSORPTION · WAVE-LENGTH · & ROTATORY POWER *in* RELATION TO MOLECULAR STRUCTURE

*SECOND EDITION*

ADAM HILGER LIMITED
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## *PREFACE*

*FOUR booklets have been issued similar in form to this one, and describing respectively the Abbe Refractometer, the Hilger Wavelength Spectrometer and Nutting Photometer, the Hilger Wavelength Spectrometer and High Resolving Power Accessories, and the Polarimeter, as made by this firm. These instruments are widely and increasingly used by chemists for the identification and estimation of substances, in the control of industrial processes, and so forth.*

*But measurements of refractive index, wave-length, absorption, and rotatory power have a deeper significance than appears in such practical applications, and it is the purpose of the present essay to remind the members of our staff and our clients how greatly the study of these properties has already contributed towards our present knowledge of the structure of matter, and what a wide and promising field it offers for further investigations.*

*The present, second edition of the essay, is a slightly amplified reproduction of its first edition published in May, 1919.*

*ADAM HILGER LTD*
*JUNE, 1920*

# REFRACTIVE INDEX
## ABSORPTION · WAVELENGTH · AND ROTATORY POWER *in* RELATION TO MOLECULAR STRUCTURE

INTRODUCTION. Everybody is familiar with the fact of the simple behaviour of light in empty space, in such regions of space, that is, from which palpable, ponderable matter has been either artificially removed or highly attenuated, or better still, in those immense interplanetary or interstellar regions where—owing to some natural conditions—there is, comparatively speaking, but very little left of it. In such empty regions or practical vacua luminous waves are propagated with constant, and for all directions the same, velocity, amounting very nearly to 300,000 kilometers, or $3.10^{10}$ cm. per second, independent of intensity or amplitude, of wave-length or colour, and of the state of polarisation. The rays of light, which in this case are generated by the normals to a wave-surface in its successive positions, are, and remain throughout, straight lines. The energy stored in light, although spreading over greater and greater regions, remains invariable in its total amount. Nor does light in empty space show any tendency to change its nature in any respect whatever, apart from the weakening of its intensity while it inundates ever-growing regions of space.

These simple properties are all more or less profoundly modified when light encounters and has to fight its way through material bodies, those marvellously complicated assemblages of atoms and molecules, themselves highly complex systems of structural elements still more minute, electrons and what not, about which modern science has only just begun to give us some reliable information. This change of propagational and other properties of light due to the presence of matter manifests itself not only in the case of those very dense aggregates known as solid and liquid bodies, but also, to a well-observable degree, in gases under ordinary



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conditions. Moreover, and this is a fact not only beautiful in itself, but of the greatest practical importance, the amount and the nature of the modification of light properties is profoundly characteristic for each kind of matter, placed under definite, controllable conditions (such as temperature and pressure or the intensity of an impressed magnetic field), in distinction from others.

## REFRACTIVE INDEX.

The most prominent, and longest known, among these changes is what is most familiar as *refraction*, at any oblique incidence, but what in its deeper aspect is best described as the change *the velocity of propagation* of light experiences in various kinds of matter, as compared with its velocity in empty space. In fact, what is called the *refractive index* of a substance is the ratio of the sines of the angles of incidence (from a vacuum or practically from air) and of refraction; this ratio is, apart from some cases in which absorption plays a very strong part, constant—*i.e.*, independent of the incidence angle—and its numerical value is equal to the ratio of the vacuum-velocity to the velocity of propagation within the substance (medium) in question. In a piece of glass, for example, of index $\mu = 1{\cdot}5$, the light velocity is but two-thirds of its undisturbed value, *i.e.*, 200,000 km. per second, and so on. And this is true either on the old-fashioned elastic theory or the now firmly established electromagnetic theory, according to which light differs from other electromagnetic waves (such as are used in wireless telegraphy) only by its considerably smaller wave-length.

Thus we can say in the literal sense of the word that a *Refractometer* enables us to measure the velocity of propagation of light in a substance, this velocity being inversely proportional to what is called the index of refraction. Now, the propagation velocity being undoubtedly the result of a very delicate and intimate reaction upon light waves of the molecules and of their configuration within the lump of matter, its value, and therefore that of the refractive index,



will stand for some very characteristic attributes of the substance in question. In fact, the refractive index, $\mu$, especially as it can now easily be measured to four or five decimal figures,* offers one of the most reliable means of identifying a substance.

It goes without saying that the value of this index depends not only upon the chemical nature of the substance, but to a considerable extent also on its temperature and pressure; these, however, can easily be controlled, and it can be said without exaggeration that the value of the refractive index, even if accurate only to four decimals, together with the temperature and pressure under which it has been obtained, are much more characteristic for a substance than, say, its specific gravity, even when measured with very refined means.

## DISPERSION.

We have hitherto spoken of *the* propagation velocity and of *the* refractive index of a substance only for the sake of shortness and in order to keep the various aspects of the action of matter upon light a little apart from one another. We should have spoken of a velocity and of an index $\mu_\lambda$ corresponding to light of a given colour or of a definite wave-length. And this brings us to the second of the subtle changes wrought in light propagation by the presence of matter. In fact, the velocity of light within material media is not only in general different from (and as a rule, to which sodium, silver, gold and copper are an exception, smaller than) that in empty space, but its value, and therefore also that of the index $\mu$, differs very considerably for different colours or wave-lengths. This beautiful phenomenon distinguishing material media from empty space is generally known by the name of *Dispersion*. What is called the dispersion curve of a substance (under given physical conditions) is the graphic representation of this property; the abscissae of the curve giving, in

* By some recent methods based upon the principles of interferometry variations of the refractive index can be detected which amount only to one-tenmillionth and less.

some conventional scale, the wave-lengths $\lambda$, and the ordinates, the corresponding values $\mu$ of the refractive index, or of some particularly interesting function of $\mu$, such as $\mu^2-1$, or perhaps $\mu^2-1/\mu^2+2$, and so on. Now if the refractive index for some chosen light quality, say the D of the sodium light, is already characteristic of a substance, its dispersion curve is still more so. Moreover, while $\mu$ itself varies considerably with the physical conditions of the substance, the dispersion curve, although not independent of such agents, retains more permanently or more tenaciously its features, and especially those singularities associated with what are known as free or natural oscillation frequencies (manifesting themselves as absorption lines or bands), and there is but little doubt that it does not merely represent properties of the whole structure, the piece of solid or the drop of liquid, but reveals to us some very intimate secrets of the individual bricks, the molecules or atoms. As such the dispersion should attract the greatest attention of the chemist as well as of the molecular physicist.

ABSORPTION. Intimately connected with the dispersion is the *Absorption* of a substance which, when carefully investigated, always turns out to be, in a more or less pronounced way, selective—*i.e.*, again dependent on the wave-length or the oscillation frequency of the impingent light. Many substances, shortly called transparent, have their absorption regions, absorption lines or bands, in the ultra-violet or the infra-red. Other substances, visibly coloured, show absorption bands (mostly very broad and without sharp limits) in the more accessible, that is, in the visible part of the spectrum. At any rate there is scarcely a substance devoid altogether of absorption; in more recent times even all such "transparent" gases as oxygen have been incontestably proved to possess well-defined absorption bands; nor do such transparent crystals as is the diamond show an exception to the rule. But what is of prime importance is that the absorption, which in its dependence



upon the wave-length can again be represented by a curve or (in pronouncedly selective cases) by a number of isolated peaks, is eminently characteristic for a substance or for a chemical group, and thus offers a most welcome supplement to the dispersion curve. Moreover, the absorption bands, and especially the finer and sharply defined lines, correspond directly to the free frequencies of a substance (attributable to a great extent to the molecules themselves, and only in part modified by the interactions within the aggregate) which mould, so to speak, the character of the whole dispersion curve. Those constants in every modern dispersion formula (of the Ketteler-Helmholtz type) which are known by the name of *free wave-lengths*, and which, in conjunction with the remaining constants, serve for the actual numerical calculation of the refraction index for any desired wave-length, represent directly the free oscillation frequencies for which the absorption is strongest.

A careful study of both the absorption and the dispersion curve of a substance will thus be seen to be a most important step towards the exploration of the intimate structure of the aggregate and, under favourable conditions, also of its molecules, and therefore of the physico-chemical aspect of a substance.

It is true that some generalisations, made chiefly by organic chemists on the great road opened by Gladstone and Dale, and by Bruehl and Landolt, associated with the names and concepts of molecular and atomic refraction, were too rash and notably too naïve. But there is undoubtedly a profound and intrinsic link or a correspondence between the dispersive and the absorptive properties on the one hand, and the structure of a molecule out of its atoms, and of these out of subatomic entities, on the other hand. The simple "additivity" of atomic refractions, those two- or three-figure numbers given in the practical chemist's tables, is certainly not the rule, but rather the exception; although it cannot be denied that it has in many cases aided and will still be helpful to the organic chemist in selecting a constitution formula among two or more otherwise equally possible ones.

But let us look more deeply and in a less sanguine manner upon the whole question. Then we shall certainly have to confess that the supposed simple additivity of optical properties is but a rough, and even very rough, first approximation to the truth, that it is actually swept away by innumerable instances of evidence of a much more delicate and immensely more complicated *constitutivity* of optical properties, the manifestation of an intricate interaction of atoms. But this is exactly the reason why we are justified in asserting that in this direction an inexhaustible field of inquiry lies open for many generations of chemists and of physicists, theorists as well as experimentalists. And the practical, technical or industrial advantages of this as of any other kind of investigations, even if originally undertaken with the purest scientific aim in view, will not fail to follow of themselves. The more complicated a class of natural phenomena appears to be, the more reason there is to investigate it with increasingly powerful and accurate instruments, aided by careful methods and cautious criticism.

## WAVE-LENGTHS OF EMISSION AND ABSORPTION SPECTRA.

In many cases the rough knowledge of the general aspect of the absorption spectrum of a substance is by itself of great service, enabling us to identify the substance in question. This means of investigation, however, as well as that based upon the emission spectra, becomes much more powerful when the *wave-length* of the spectrum lines is measured. This has in recent times become an extremely accurate process, enabling us to measure the wave-length of a well-defined, sharp line to one-hundredth or—in the case of comparisons or shifts (St. John, Evershed)—even to a few thousandths of an Ångström unit, *i.e.*, of a few thousandths and perhaps even down to one-thousandth of $10^{-8}$ cm. Such accurate measurements require, of course, a particularly refined and costly apparatus; but even those easily accessible *wave-length spectrometers* which enable one to discern



and to measure 2 or 3 Å.U. (about ½ distance of the familiar two D-lines of sodium), offer many new possibilities in the field of optical investigation of substances. The wave-length which, if originally measured in air, can easily be reduced to its vacuum-value $\lambda$ (for this purpose good tables are available), gives us directly the natural or free period, $T$, of oscillations of the emitting or the absorbing atoms or molecules; for, if $c$ be the standard or empty-space velocity of light, we have simply $\lambda = cT$. While the first-mentioned optical properties, such as the refractive index for a given wave-length, are to a great extent the outcome of an entangled co-operation of a great number of molecules composing a lump of matter, the spectral lines of emission or of absorption, especially of gases, are the work of the individual molecules, or even atoms,* but very slightly, if at all, modified by the interaction of neighbours. A spectrum line with its accurately measured wave-length is thus the most direct manifestation of the intrinsic properties of a molecule, and even of its component atoms; for the lines (and also many features of their distribution) of a chemical element are still recognisable in the spectra of its various compounds.

Apart from slight shifts due to strong pressure variation, the spectrum, consisting in the majority of cases of an amazing number of separate lines, visible and ultra-violet or infra-red, is also one of the most *permanent* properties or manifestations of a substance or, better, of its component particles. Under such circumstances it is manifestly impossible to overrate the physico-chemical importance of the quantitative investigation of the emission- and the absorption-spectra of substances.

While in the case of refractivity and of dispersion the physico-chemists, notably those of the Landolt-Bruehl school,

* The intensity or the amount of emitted or absorbed light is, of course, due to the minute contributions of many individual oscillators, but the period $T$, and therefore also the measured wave-length, belongs to each of them taken separately. And, to judge from the extreme fineness of the lines, especially if (in the case of complex ones) ultimately split by a Lummer plate, the individual differences of period, if at all existing, are extremely small.

aimed from the beginning at a quantitative representation of the properties of compounds by means of the additivity law, of a handful of more or less provisional atomic refractions or "refractive equivalents," and of various extra-terms, such as those due to double or treble bonds, of "exaltations," and so on, their line of research concerning emission and absorption spectra has assumed a more qualitative character. The results are here, on the whole, stated with more criticism and caution, and it would seem that, owing perhaps to the latter circumstance, the results hitherto gathered, although not professing to be a mathematical synthesis and prediction of numerical coefficients, are, comparatively speaking, very valuable. The tangible result of a long series of investigations aiming at a discovery of the relations between absorption spectra and the chemical constitution of mainly organic compounds, dating from 1879 (Hartley), consists in a wealth of absorption curves (relative layer thickness plotted against oscillation frequency) of many substances. One of the most characteristic features of the conclusions which it was possible to draw from these experimental data is that, in the ultraviolet and the visible regions of the spectrum, the absorption is eminently constitutive, the only ascertainable trace of "additivity" consisting in the effect of what is called "weighting the molecule," when the absorption bands are shifted towards the less refrangible end of the spectrum. According to Drude's (electronic) theory the longer, infra-red, natural oscillation periods belong to the whole atoms, not to the sub-atomic electrons, as vibrators. In conformity with this theoretical conclusion the infra-red absorption should exhibit some additive features; and, in fact, Abney and others were able to detect certain permanent or almost permanent bands "due to" hydrogen, carbon, and hydroxylic oxygen. Again, a valuable feature, already enunciated as a general rule by Hartley, and more recently confirmed in many new and subtle cases, is that chemical compounds of closely allied structures have similarly shaped absorption curves. The pushing of the bands towards the red by the addition of certain groups to some (not too complicated) compounds



seems also to be a well-established effect. A number of other more special regularities have, no doubt, been correctly observed and tabulated. But it is undeniable that infinitely more remains yet to be done in this vast and promising domain of physico-chemistry. New fields of vital interest and of a peculiar charm have also been opened for high-precision spectroscopy (especially of emitted spectra) by the several triumphs of Bohr's new theory of spectra (1913), based on Planck's concept of *quanta*, and enriched by Sommerfeld's theory of the *fine structure* of spectrum "lines" or, rather, groups with all their marvellous intricacies—a domain bristling with new, difficult, yet most attractive problems for the experimental as well as the theoretical spectroscopist.*

## ROTATORY POWER.

The intimate relation of the natural (as distinguished from the magnetic) *Rotatory power* of a substance with the space-configuration of the atoms within its molecules was already suspected and even fully grasped in its deeper aspect by the great Pasteur (1848), who has deserved well of humanity in another more familiar field.

As was mentioned at the outset, light propagated in vacuo does not experience any change of its state of polarisation. Thus, for instance, rectilinearly polarised light remains so and the plane of polarisation—containing the magnetic and perpendicular to the electric force—is preserved throughout the course of the waves; more generally, if the light be elliptically polarised, the axes of the ellipse retain their orientation—*i.e.*, remain at their successive positions parallel to themselves. This is still the case in common media such as air, or water, glass, and so on, which differ optically from a vacuum only by their refractive, dispersive and absorptive power. But certain crystals (having no symmetry plane), and notably quartz, possess the remarkable property of rotating the plane of polarisation of light *pari passu* with

* A first acquaintance with this beautiful domain of modern spectroscopic researches may be obtained from my *Report on the Quantum Theory of Spectra*, just published (May, 1920), by Adam Hilger, Ltd.

its propagation; a quartz plate of 1 mm. thickness, cut perpendicularly to the crystal's optical axis, turns the plane of polarisation of D-light through as much as 21° 43′ (and of violet light, in the neighbourhood of the hydrogen line, H, even through somewhat more than 51°). Of course, in such crystalline, active bodies the amount of rotation depends, *cæteris paribus*, on the orientation of the wave-normal, and the phenomenon, although conditioned, no doubt, by some properties of the molecules, is essentially influenced by the manner in which they are arranged in the crystal.

There is, however, a vast number of non-crystalline, isotropic substances, such as turpentine and the most familiar sugar solutions, which, although in a much weaker degree than quartz, are also endowed with "natural activity" or rotatory power easily detectable and measureable, some dextrogyrous, others levogyrous—*i.e.*, right- and left-handed. It is this, macroscopically speaking, *isotropic* class of naturally active substances, in which therefore no direction of propagation is privileged, that is most particularly interesting from the physico-chemical point of view, for owing to the complete absence of macroscopic structural regularity of the whole aggregate (a liquid or a liquid solution), the rotatory effect in such substances is manifestly attributable to its building stones, pointing, that is, to some sort of intrinsic chirality of its separate molecules.

A first hint as to the possible nature of this peculiarity of the molecules of active substances was given by Pasteur's discovery of an instance of the phenomena now known under the head of *optical isomerism*. In 1848 Pasteur found that besides the already known dextrogyrous tartaric acid there exists a levogyrous one, a substance, that is, isomeric with the former acid, and coinciding with it completely in all chemical points, the only difference being that solutions of the two isomeric acids turned the polarisation plane *in opposite senses*, and—what is equally remarkable—*cæteris paribus*, through *the same angle*. Moreover, the salts of these two acids had, correspondingly, a right- and a left-hand hemihedral crystal face. This led Pasteur to assume an *asymmetric*



*arrangement of atoms* within each of the two isomeric molecules, the features of the arrangement being irreconcilably different for the two kinds of molecules. But there was no such possibility in the bidimensional, planar formula universally adopted by the chemists of those days. Pasteur made therefore the bold leap into the third dimension, pointing out—for the first time—the possibility of explaining the phenomena of optical isomerism by a *three-dimensional* arrangement of atoms, and consequently by the use of three-dimensional constitution formulæ. This was a step on the path of progress whose importance it is impossible to overrate. Pasteur even stated the true relation of the isomeric molecules, by describing it (1860) as "an asymmetric arrangement of atoms of such a kind as cannot be superposed upon its mirror-image," one of such configurations belonging, say, to the molecule of the dextrogyrous acid and its exact image to that of the levogyrous acid.

Other instances of optical isomerism, exhibiting exactly the same features, were discovered (1873) by Wislicenus, and the next year saw the definitive inauguration, in almost simultaneous papers by van't Hoff and Le Bel, of *Stereo-chemistry*.

Stereo-chemical investigations centered at first almost exclusively round the carbon compounds, the prominent heuristic concept being the asymmetric carbon atom. But in more recent times such investigations have been extended to other elements, to nitrogen, and also to sulphur, selenium and tin. It would carry us much beyond the scope of the present little essay to describe the many triumphs of stereo-chemistry which, moreover, can be looked up in good and easily accessible monographs on the subject. We shall, therefore, limit ourselves to pointing out that these successes have, hitherto, at least, consisted not so much in calculating beforehand (as in the case of refractivities) the numerical value of the specific rotatory power of a compound, as in the prediction of the possibility of new stereo-isomeres and in their actual discovery or synthesis guided by such theoretical prediction. Thus, to quote only one of the most striking examples, all the ten stereo-isomeric forms of a certain com-

plicated kind predicted theoretically by van't Hoff were experimentally found embodied in as many saccharic acids (Emil Fischer), to wit, eight active forms and two inactive ones, in perfect agreement with theoretical expectation.

The vast field of even these qualitative, stereo-chemical researches aided by optical observation is, undoubtedly, yet far from being exhausted, and should as such engage the keenest interest of the chemist and the physicist.

Concerning the amount of rotation or the value of the specific rotatory power practically nothing has hitherto been achieved, the formula proposed (about 1890) by Guye and by Crum Brown—representing the rotatory power as proportional to the product of all the six differences of the molecular weights of the four groups united to the carbon atom—lacking not only any plausible theoretical support, but also failing to cover even coarsely the facts of quantitative experience. Quite recently an interesting and deeply reaching theory of natural rotation, on electro-magnetic lines, has been proposed by Oseen. This attempt seems very promising, but requires for its completion still much work on both the theoretical and the experimental sides. The older roughly sketched electron theory of the rotatory power given by Drude accounts for the essential features of the phenomenon without entering into the structural details of the molecular systems. This theory gives for the *dispersion* of rotatory power formulæ of the Helmholtz type in which the natural periods are those belonging to what are called the "active" electrons. To a first approximation these formulæ reduce to the well-known empirical formula of Biot (rotatory power inversely as $\lambda^2$) which for many cases is sufficient. For larger portions of the spectrum the full formulæ of Drude represent the observations much more accurately than Biot's, and even excellently—as, for instance, in the case of quartz from 0·219 up to 2·14 microns.* They cover also the cases of anomalous rotatory dispersion observed in absorbing organic liquids. A further development of even this rough electrical theory and the comparison of its results with obser-

* A micron is one-thousandth of a millimetre or 10,000 Å.U.



vations would not be without value for the exploration of the interior of molecules and of atoms, especially as it sheds some interesting light upon the "active" or "rotatory" electrons, which in general appear as distinct from those responsible for the ordinary dispersion and absorption phenomena. An important quantitatively additive property relating to compounds containing two or more asymmetric carbon atoms which was already announced by van't Hoff (1875) has more recently been verified experimentally in a very satisfactory manner. It asserts that the rotatory power of such a compound is equal to the algebraic sum of the powers due to the separate "asymmetric carbon atoms" together, of course, with their satellites. This so-called law of optical superposition seems to be the only notable consolation of the "additivity" hunter in this beautiful domain of optical phenomena. It is, no doubt, based upon a rather loose association of the two or more component parts of the whole compound. The intrinsic physics of each of them as a system is still awaiting its thorough investigation. If an ultimate reduction to atoms is aimed at, the phenomenon of natural rotation of the plane of polarisation is manifestly a *constitutive* one *par excellence*. But the more it is so, the more active attention of the physico-chemist does it deserve.

Last, not least, the rotatory power of organic compounds seems also to open a very promising field for the biologist owing to the well-established selective attitude of certain living organisms or of their enzymes towards stereo-isomeres, a class of phenomena already discovered and utilised by Pasteur himself, and more recently studied by Emil Fischer and others. According to the latter's simile, in order that an enzyme may successfully attack one of two enantiomorph molecules, there must be between the aggressor and its victim some similarity of intramolecular configuration, somewhat as between "lock and key." But the very appeal to this, no doubt, most happy comparison will serve to remind the modern bio-chemist how much remains still to be done in the rich field of this class of phenomena.

*May*, 1920. *L. SILBERSTEIN.*

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